

# AT ENTERPRISES AND INSTITUTES

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## DISSOLUTION OF CRISTOBALITE IN GRANODIORITE AND FELSITE MELTS

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The process of dissolution of cristobalite during the calcination of acid-resistant articles based on Buskul'skoe clay using granodiorite and felsites is simulated. The mechanism governing the dissolution of cristobalite in their melts is determined. The process of dissolution of cristobalite in felsite and granodiorite melts can be divided into two stages. First, for short holding times, the rate of dissolution is determined by the rate of silicate formation during the interaction of the melt, formed by heating felsite or granodiorite, with cristobalite. Second, for long holding times, the rate of dissolution is determined by the rate of diffusion, the rate of dissolution decreasing substantially.

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In acid-resistant articles based on clay from the Uskul'skoe deposit, using Severovskoe granodiorite or Pokrovskoe felsites as fluxes, silica is in the form of quartz and cristobalite. After calcination the amount of quartz present in the clay, granodiorite, and felsites decreases as a result of dissolution or being converted into cristobalite. The latter is also formed from amorphous alumina when clayey minerals decompose. The quartz in acid-resistant materials does not degrade the quality of articles, while cristobalite increases the CLTE and permeability and decreases their strength and acid-resistance. The dissolution of quartz and cristobalite in the melt during calcination increases the acid-resistance of the glass phase. The process resulting in the formation of cristobalite is most critical in the technology used to produce acid-resistant brick. The properties of the articles largely depend on the content of cristobalite and therefore on the dissolving power of the liquid phase with respect to silica arising when acid-resistant materials are calcined.

A series of samples was fabricated from granodiorite with cristobalite (1 : 1) and felsite with cristobalite (1 : 1) for the purpose of simulating the process of dissolution of cristobalite during calcination of Buskul'skoe clay with fluxes added. As a result of the complexity of the separation of the cristobalite from the calcined clay, the cristobalite was introduced into the mix in the form of a powder obtained by calcinating hydrous silicic acid (GOST 4214–78) at 1250°C

in 6 h. XPA revealed one crystalline phase in such material — cristobalite.

The powders of the initial components of the mix with dispersity no greater than 0.063 mm were mixed in dry form and carefully ground in a ceramic mortar. In preparing the mixes, polyvinyl alcohol was used as a binder. Cylindrical samples, 20 mm in diameter and 10 mm high, were compacted from the mix under pressure 40 MPa. The samples formed were dried at 100°C and then sintered at 1000, 1150, and 1300°C with temperature increased at the rate 400 K/h. The content of the cristobalite and quartz in the samples was determined by quantitative x-ray phase analysis (Table 1).

The content of cristobalite and quartz in the samples with granodiorite and felsite starts to decrease during sintering at 1000°C and continues as this temperature increases; this is due to the dissolution of silica in the alkali-silicate melt, which forms when granodiorite or felsite is heated. XPA did not show any new crystalline phases in the samples.

It is well-known that the dissolution of silica in silicate melts of glass mixes is a heterogeneous reaction, which is governed by diffusion kinetics [1–3], according to which the most active ions diffuse from the melt to the surface of the quartz grains, where the chemical reaction forming silicate occurs. The SiO<sub>2</sub>-containing products of the reaction are removed by diffusion mass transfer between the layers of melt forming around grains and containing silica with different concentrations, glass mass filling the rest of the volume. It has also been determined that the process of dissolution of

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TABLE 1.

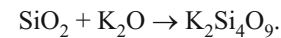
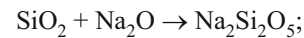
Sintering temperature, °C	During, min	Mass content, %			
		cristobalite		quartz	
		in felsite	in granodiorite	in felsite	in granodiorite
1000	0	39	41	15	9
	30	38	39	15	9
	60	37	38	15	9
	120	37	37	15	9
	180	37	37	15	9
	240	37	36	15	9
1150	0	37	30	13	6
	30	35	25	10	5
	60	32	24	10	5
	120	30	24	10	4
	180	30	24	8	4
	240	30	22	9	4
1300	0	30	21	8	3
	30	28	17	5	2
	60	25	16	5	2
	120	23	14	4	2
	180	23	14	4	1
	240	22	13	3	1

quartz in porcelain is also due to the diffusion of alkali and other elements of the melt, which form alkali-silicate glass [4]. Quartz dissolves and in the process its crystalline structure is destroyed. The dissolution of cristobalite during sintering of acid-resistant articles has not been adequately studied.

Felsite and granodiorite, whose chemical compositions are presented in Table 2, are introduced into acid-resistant mixes as fluxes. The temperatures of the eutectics on heating granodiorite and felsites (the main minerals) were calculated by the method of [5] taking account of their melting temperature. The dissolution of cristobalite in ceramic materials starts with the appearance of a liquid phase during sintering. For heating granodiorite, the computed minimum temperature of the eutectic is 1011°C and lies in the system albite – pargasite – orthoclase; for heating felsites, the minimum

temperature of the eutectic is 1026°C and lies in the system albite – orthoclase. In reality, the mineral composition of granodiorite and felsites is much more complicated. Biotite, epidote, amphibole, sphene, apatite, magnetite, zircon, muscovite, and other minerals are present in granodiorite [6]. Aside from feldspars, quartz, and kaolinite, felsite contains sericite and limonite. XPA shows that when granodiorite and felsites are heated a liquid phase appears in the temperature interval 950 – 1100°C.

The main cations, forming the melt, in the systems silica – granodiorite and silica – felsites are  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . The cations  $\text{Si}^{4+}$  in the glass structure are glass formers;  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  are modifiers;  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are interstitial ions [7]. Silicon forms the strongest chemical bond with oxygen; potassium and sodium form the weakest bond. Consequently, the dissolution of cristobalite and quartz in melt occurs as a result of the diffusion of potassium and sodium ions to the silica surface, where they form the low-melting potassium and sodium silicates according to the reactions



Layers of silicate melt with different silica concentration form around silica particles. When silica dissolves the viscosity of the melt increases as a result of the formation of bridge oxygen atoms and an increase of the fraction of Si – O bonds, which are several-fold stronger than Me – O (Me — K, Na) bonds. The presence of alkali-earth metals in alkali-silicate melt results in a decrease of the viscosity of the melt. Calcium oxide acts more strongly than magnesium oxide.

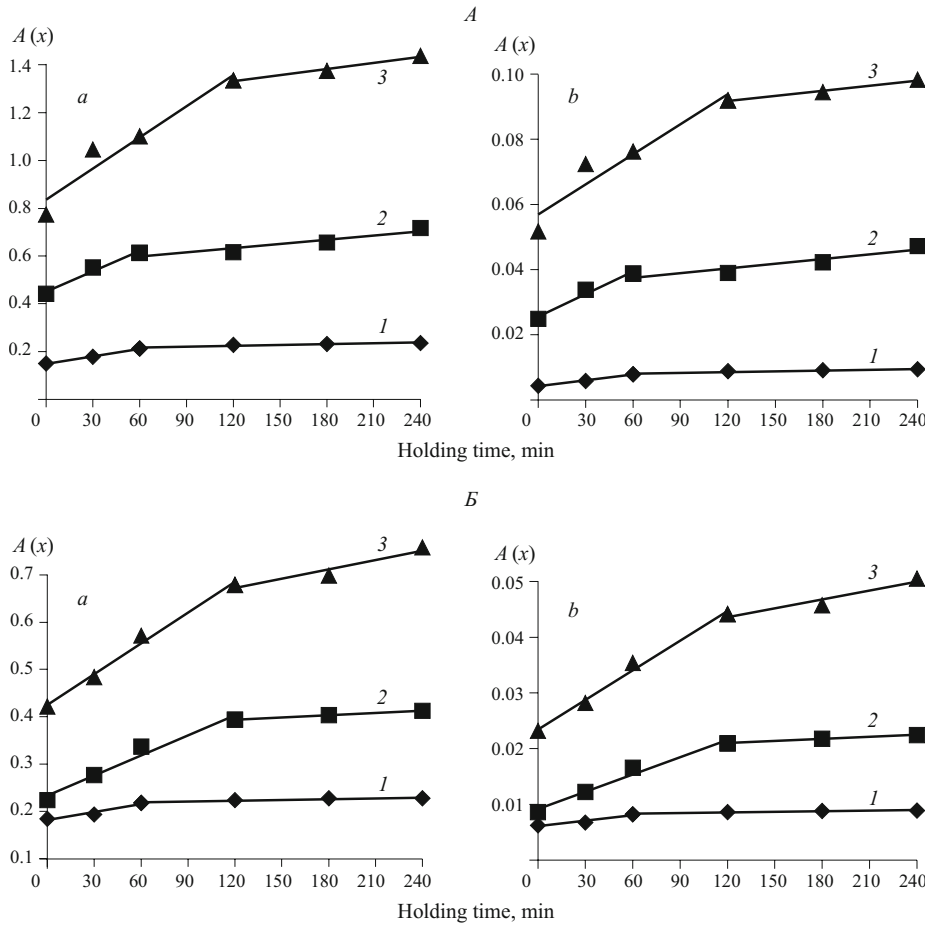
#### Strength of the Me – O Bond (According to A. A. Appen)

Element	Bond strength, kJ/mole
Si . . . . .	443
Ca . . . . .	134
Mg . . . . .	155
K . . . . .	54
Na . . . . .	84
Al . . . . .	335 – 423 for CN* = 4 224 – 284 for CN = 6

\* CN) coordination number.

TABLE 2.

Component	Mass content, %									
	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	CaO	MgO	$\text{TiO}_2$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	calcination losses	$\text{SiO}_{2(\text{free})}$
Granodiorite	65.92	15.26	3.67	4.05	1.89	0.45	1.75	5.82	0.86	20.0
	66.68	15.43	3.71	4.10	1.91	0.45	1.77	5.88	—	20.0
Felsite	75.93	13.17	1.32	0.24	0.05	0.06	3.84	3.53	1.93	35.0
	77.42	13.43	1.35	0.24	0.05	0.06	3.91	3.60	—	20.0



**Fig. 1.** Degree of dissolution of cristobalite in granodiorite (*A*) and felsites (*B*) versus the holding time at temperatures 1000°C (*1*), 1150°C (*2*), and 1300°C (*3*): *a* and *b*) calculation using Eqs. (1) and (2), respectively.

The process of silicate formation is limited by the reaction rate itself. The following equation is valid for the process [8]:

$$A(x) = (1 - x)^{-2/3} - 1 = k' \tau, \quad (1)$$

where  $x = \Delta C / C_{\text{ini}}$  ( $\Delta C$  is the change of the content of cristobalite during the sintering process;  $C_{\text{ini}}$  is the initial content of cristobalite);  $x$  is the degree of completion of the dissolution process (degree of conversion);  $k'$  is the rate constant of the chemical reaction; and,  $\tau$  is the isothermal holding time.

For diffusion processes, the Ginstling–Brounshtein equation holds:

$$A(x) = 1 - (1 - x)^{2/3} - \frac{2}{3}x = k'' \tau, \quad (2)$$

where  $k''$  is the rate constant of the reaction associated with the diffusion coefficient.

The rate constant for the reaction of dissolution of silica in melt depends on the temperature and can be calculated from the Arrhenius equation:

$$k = A \exp\left(-\frac{Q}{RT}\right), \quad (3)$$

where  $A$  is the pre-exponential factor;  $Q$  is the activation

energy of the dissolution process;  $R = 8.3144 \text{ J/(K} \cdot \text{mole)}$  is the gas constant; and,  $T$  is the absolute temperature, K.

Taking the logarithm, Eq. (3) becomes

$$\log k = \log A - \frac{Q}{RT}.$$

Figure 1*A* shows that the degree of dissolution of cristobalite in granodiorite melt versus the calcination time, determined by the rate of silicate formation (*a*) and the rate of diffusion (*b*), and Figure 1*B* shows the dependence of the dissolution of cristobalite in felsite melt versus the calcination time. An inflection is seen in the curves. For dissolution of cristobalite in granodiorite melt at 1000 and 1150°C the inflection point corresponds to holding time 60 min and at 1150 and 1300°C to 120 min. The inflections on the curves  $A(x) = f(\tau)$  attest to the decrease of the reaction rate, which is due to the change of the mechanism of the reaction flow or a change of the dominant process.

Thus, the rate of dissolution of cristobalite is initially limited by the rate of silicate formation (before the inflection point) and then, at the second stage, by the rate of diffusion mass transfer between the melt layers surrounding cristobalite grains with different silica concentration and the rest of the granodiorite or felsites melt volume (after the inflection

point). It cannot be asserted that only the process of silicate formation occurs at the first stage and only diffusion at the second stage. Most likely, both processes proceed simultaneously with the difference that chemical interaction of the melt with cristobalite as well as diffusion associated with the process of equalization of the silica concentration in the melt occur at the first stage while at the second stage supersaturation of the melt with silica around the cristobalite particles occurs and the rate of the chemical interaction decreases. The subsequent decrease of the rate of the chemical reaction is due to the decrease of the diffusion rate because of the high viscosity of silica-enriched melt.

The rate constants for the dissolution of cristobalite in granodiorite and felsite are presented in Table 3. As temperature the calcination increases, the rate of dissolution of cristobalite increases as a result of a decrease of the viscosity of the melt and decreases as the holding time increases, since the silica content in the melt increases.

The rate constants for the dissolution of cristobalite in granodiorite and felsite melts are determined according to the relation  $\log k - (1/T) \times 10^3$ . The activation energies of the silicate formation and diffusion processes were calculated (Table 4).

The dissolution rate of cristobalite in granodiorite melt is higher than in felsite melt at the initial and second stages. The activation energy for the dissolution of cristobalite in felsite melt is higher than in granodiorite melt; this is due to the higher content of oxides-fluxes and lower content of quartz in granodiorite than in felsite. The degree of dissolution of cristobalite with cristobalite : granodiorite = 50 : 50 is 27.1% at 1000°C, 55.6% at 1150°C, and 73.7% at 1300°C, while for the same ratio cristobalite : felsite the indicated reaction proceeds to degree of completion 26.5% at 1000°C, 40.4% at 1150°C, and 57.1% at 1300°C. Considering that the dispersity of the granodiorite, felsite, and cristobalite powders is the same and represented by particles smaller than 0.063 mm, the completeness of the dissolution of cristobalite in granodiorite and felsite depends more on the temperature than on the calcination time of the samples. The optimal holding time is 120 min, and longer times do not result in a substantial transfer of cristobalite into the melt.

In summary, cristobalite dissolves more intensively in granodiorite than in felsite melt, since when granodiorite is heated a melt that is more aggressive with respect to silica is formed than in the case of felsite. Increasing the calcination temperature likewise increases the solubility of cristobalite

TABLE 3.

Calcination temperature, °C	Rate constant of the cristobalite dissolution process $K \times 10^3$			
	in granodiorite, determined by the rate of		in felsite, determined by the rate of	
	chemical interaction	diffusion	chemical interaction	diffusion
1000	1.0000	0.0080	0.6000	0.0004
1150	2.8000	0.0500	1.4000	0.0100
1300	4.3000	0.0500	2.2000	0.0500

TABLE 4.

Indicator	Reaction rate constants and activation energy			
	granodiorite in the region of		felsite in the region of	
	chemical interaction	diffusion	chemical interaction	diffusion
Reaction rate constant	– 4.2740	– 5.479	– 5.0048	– 7.2243
Activation energy of the dissolution of cristobalite in melt, kJ/mole	81.7	104.8	95.7	138.1

in granodiorite and felsite. The dissolution of cristobalite and quartz in melt increases its viscosity and acid-resistance. An increase of the viscosity of the melt, on the one hand, decreases the homogenization of the materials on calcination and, on the other hand, decreases the deformation of the articles during calcination.

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